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RESEARCH IN THE CHEMISTRY OF HETEROCYCLIC QUINONEIMINES.
4.* EFFECT OF MODE OF ACTIVATION OF THE REAGENTS ON THE REACTION OF 3-PHENOTHIAZINONE WITH ALKANETHIOLS

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2-Alkylthio- and 2,4-dialkylthio-3-phenothiazinones were obtained in the case of activation of 3-phenothiazinone in reactions with alkanethiols. Activation of the reagent by means of a charge accelerates the reaction significantly and is accompanied by the additional formation of 1,2-dialkylthio-3-phenothiazinones.

It is known that the mode of activation of the reagents may have a substantial effect on both the rate of a reaction and its regioselectivity [2, 3]. Depending on the type of nucleophile, the substitution of a hydrogen atom in a series of heterocyclic quinoneimines may proceed under conditions of activation of either the substrate or the reagent. In a number of cases only one of the indicated modes of activation proves to be effective. Thus 3-phenothiazinone does not react with alcohols but forms alkoxy derivatives smoothly with alkoxides [4].

The high nucleophilic reactivities of thiols and thiolate anions with respect to various substrates [5] in conjunction with the possibility of subsequent transformations of the resulting alkylthio derivatives makes them advantageous as reagents in the study of the various nucleophilic processes [2].

We have investigated the reaction of 3-phenothiazinone with a number of aliphatic thiols and the corresponding thiolates. Under conditions of activation of the substrate (H^+) the reaction of 3-phenothiazinone (I) with thiols proceeds smoothly at 0°C. The initially formed mixture of colorless products of addition and reduction of 3-phenothiazinone is oxidized in air to mono- and dialkylthio-3-phenothiazinones and starting I. The principal products of the reaction of 3-phenothiazinone with thiols are 2-alkylthio-3-phenothiazinones (II). For example, in the case of octanethiol (an eight- to tenfold excess) the ratio of 2-octylthio-3-phenothiazinone and 2,4-dioctylthio-3-phenothiazinone is ∿8:1. The overall yield

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*See [1] for Communication 3.

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may approach the quantitative level based on 3-phenothiazinone. Judging from thin-layer chromatography (TLC), 2-alkylthio-3-phenothiazinones do not give even traces of 2,4-disubstituted compounds with excess thiol under conditions of reaction with 3-phenothiazinone, and the formation of 2,4-dialkylthio-3-phenothiazinones from the 4-monosubstituted compounds can therefore be regarded as more likely.

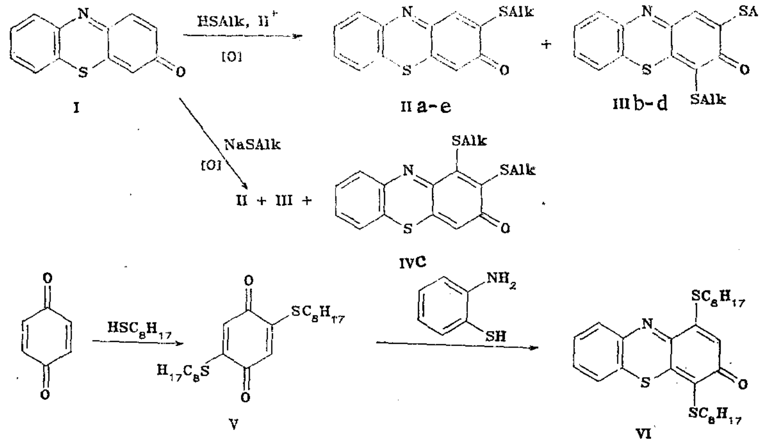
The reaction of 3-phenothiazinone with thiolates in air proceeds instantaneously and is not accompanied by the appreciable formation of colorless dihydro compounds. 2-Alkylthio-3-phenothiazinones are also the principal products; however, in contrast to the reaction with thiols, 1,2-disubstituted IV dominate in the disubstitution products, and 2,4-dialkylthio derivatives III are formed in smaller amounts. The reaction of 3-phenothiazinone with sodium octylthiolate leads to 2-mono-, 1,2-di-, and 2,4-dioctylthio-3-phenothiazinones in a ratio of ∿9:2:1.

Two singlets of the protons in the 1 and 4 positions of the quinoneimine fragment at 7.5 and 7.0 ppm, respectively, are observed in the PMR spectra of 2-alkylthio-substituted II. The PMR spectra of 2,4-disubstituted III contain one singlet of a 1H proton at 7.5 ppm, which was assigned on the basis of a comparison with the chemical shifts of the protons of the quinoneimine fragment of unsubstituted 3-phenothiazinone [6]. The singlet at 7.0 ppm was similarly interpreted in the establishment of the structure of a 1,2-dialkylthio-3-phenothiazinone. The PMR spectra of II, III, and IV contain an identical multiplet of protons of the aromatic part of the molecule at 7.5-8.2 ppm. The existence of disubstitution in III and IV is confirmed by the integral intensity of the signals of the protons of the alkylthio substituents and by the results of elementary analysis.

To confirm the structure of dialkylthio-3-phenothiazinones III and IV we obtained a dialkylthio-3-phenothiazinone with alternative structure VI with substituents in the 1 and 4 positions by condensation of o-aminothiophenol with 2,5-dioctylthiobenzoquinone (V). 2,5-Dioctylthiobenzoquinone (V) was obtained in turn by the method in [7] from benzoquinone and octanethiol, and its structure was confirmed by PMR spectroscopy. The PMR spectrum of V contains a singlet of two equivalent protons at 6.35 ppm and signals of protons of two octyl groups. The PMR spectrum of 1,4-dioctylthio-3-phenothiazinone, which was synthesized by the method described above, contains a multiplet of aromatic protons of the aromatic part of the molecule at 7.4-8.1 ppm, which was identical to that observed for II, III, and IV; however, the singlet of the proton of the quinoneimine fragment is found at stronger fields at 6.6 ppm.

Absorption bands of the system of conjugated C=O, C-C, and C-N bonds of the quinoneimine fragment at 1590-1630 cm^{-1} are observed in the IR spectra of II-IV and VI; an absorption band of an OH group at 3430 cm^{-1} is present in the spectrum of IIe.

The absorption maxima of II and III in the visible region have a small hypsochromic shift relative to unsubstituted 3-phenothiazinone; a shift of the absorption maximum in the visible region relative to I is virtually completely absent in the spectrum of 1,2-dioctylthio-substituted IV. 1,4-Dioctylthio-3-phenothiazinone (VI) is more deeply colored than II-IV and has two absorption maxima at 433 and 575 nm in the visible region.



a Alk=*i*-C$_3$H$_7$; b Alk=C$_4$H$_9$; c Alk=C$_8$H$_{17}$; d Alk=C$_{10}$H$_{21}$; e Alk=CH$_2$CH$_2$OH

Thus the mode of activation of the reagents has a substantial effect on the reaction of 3-phenothiazinone with thiols. The use of thiolates makes it possible to increase the

TABLE 1. Alkylthio-3-phenothiazinones

Compound	mp, °C	R_f (chloroform)	λ_{max}, nm	Found, %				Empirical formula	Calculated, %				Yield, g/g of starting 3-phenothiazinone
				C	H	N	S		C	H	N	S	
IIa	138—140	0,45	460	62,8	4,8	4,8	22,9	$C_{15}H_{13}NOS_2$	62,7	4,6	4,9	22,4	0,4—0,5
IIb	134—135	0,5	460	63,7	5,0	4,6	21,3	$C_{16}H_{15}NOS_2$	63,7	5,0	4,6	21,3	0,4—0,5
IIc	104—106	0,55	460	67,1	6,6	4,0	17,5	$C_{20}H_{23}NOS_2$	67,2	6,5	3,9	17,9	0,5—0,7
IId	90—92	0,57	460	68,4	7,2	3,8	16,6	$C_{22}H_{27}NOS_2$	68,5	7,1	3,6	16,6	0,5—0,7
IIe	178—180	0,04	460	58,1	3,9	4,5		$C_{14}H_{11}NO_2S_2$	58,1	3,8	4,8	22,1	0,4—0,5
IIIb	82—84	0,72	466	62,6	5,8	3,7	24,5	$C_{20}H_{23}NOS_3$	62,6	6,0	3,6	24,7	0,05—0,1
IIIc	58—60	0,88	465	67,4	8,1	2,3	19,5	$C_{28}H_{39}NOS_3$	67,0	7,8	2,8	19,2	0,05—0,1
IIId	48—50	0,91	463	68,8	8,9	3,0	17,2	$C_{32}H_{47}NOS_3$	68,9	8,5	2,5	17,2	0,05—0,1
IVc	122—124	0,83	506	66,8	7,8	2,7	19,1	$C_{28}H_{39}NOS_3$	67,0	7,8	2,8	19,2	0,1—0,3
VI	50—52	0,9	575	66,9	7,9	2,9	19,2	$C_{28}H_{39}NOS_3$	67,0	7,8	2,8	19,2	—

reaction rate significantly; however, the regioselectivity of the reaction decreases in this case. The high nucleophilicities of thiols and thiolate ions and their ability to undergo transformations with the participation of radical intermediates evidently explain the possibility of the formation of 4-substituted derivatives of 3-phenothiazinone, the incorporation of substituents in which has been noted for radical reactions [6, 8]. It is interesting that thiolates, like alkoxides [4], are capable of substitution of the hydrogen atom in the 1 position of the 3-phenothiazinone molecule, although the formation of even traces of 1-substituted compounds is not observed under conditions of activation of the substrate (reactions with thiols and aryl- and alkylamines) [9, 10]. The reaction of 3-phenothiazinone with thiols and thiolates is not accompanied by substitution of the hydrogen atom in the 7 position of the aromatic fragment of the molecule, whereas the formation of 7-substitution products has been established for many reactions of 3-phenothiazinone and 3-phenoxazinone with nucleophiles [4, 9-11].

EXPERIMENTAL

The PMR spectra of solutions of the compounds in chloroform were recorded with a Perkin-Elmer R-12B spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The electronic spectra of solutions in ethanol were obtained with a Specord UV-vis spectrophotometer. The IR spectra of mineral oil suspensions of the compounds were obtained with a UR-20 spectrometer. The purity of the compounds obtained was monitored by thin-layer chromatography (TLC) on Silufol-254 plates by elution with chloroform.

Alkylthio-3-phenothiazinones (IIa-e, IIIb-d, IV). A) Reaction of 3-phenothiazinone with thiols. Two to three drops of concentrated HCl and an eight- to tenfold excess (with respect to the equimolar value) of the thiol were added with stirring to a solution of 1 g (5 mmole) of 3-phenothiazinone in 50 ml of tetrahydrofuran (THF). After a few minutes, the solution became colorless, and it was then stirred at room temperature for 10-12 h as air was bubbled through it. The degree of conversion of 3-phenothiazinone was monitored by TLC. When necessary, more thiol was added. At the end of the reaction, the solvent was removed by distillation, and the residue was dissolved in chloroform. The first (brown), second (orange), and third (crimson) fractions were collected, and the eluent was evaporated to give 2,4-dialkylthio- and 2-alkylthio-3-phenothiazinones and starting I, respectively.

B) Reaction of 3-phenothiazinone with thiolates. A five- to sevenfold excess of the sodium salt of the thiol was added with vigorous stirring to a solution of 1 g (5 mmole) of I in 50 ml of THF, during which the color of the solution changed from red to brown. In the case of incomplete consumption of the 3-phenothiazinone more thiolate was added, after which the solvent was removed by distillation, and the residue was dissolved in chloroform and chromatographed as in method A. The first (brown), second (red), third (orange), and fourth (crimson) fractions were collected, and the eluent was removed to give 2,4-dialkylthio-, 1,2-dialkylthio-, and 2-alkylthio-3-phenothiazinones and a certain amount of 3-phenothiazinone, respectively. Compounds II-IV were crystallized from acetone; their characteristics are presented in Table 1.

2,5-Dioctylthiobenzoquinone (V). This compound was obtained by the method in [7] from benzoquinone and octanethiol. The structure of V was confirmed by PMR spectroscopy (see above). The yellow-orange crystals had mp 143-145°C.

1,4-Dioctylthio-3-phenothiazinone (VI). A 0.12-g (1 mmole) sample of o-aminothiophenol was added with stirring to 0.35 g (1 mmole) of dioctylthiobenzoquinone V dissolved in 20 ml of anhydrous pyridine, and the mixture was heated to 100°C and allowed to stand for 1 h. It was then diluted with 100 ml of water, and the precipitate was removed by filtration, dried, and dissolved in 20 ml of chloroform and chromatographed on silica gel (100-250 μm) by elution with chloroform. The first (green) fraction was collected, and the eluent was evaporated to give 0.3 g (64%) of dark acicular crystals. The characteristics of VI are presented in Table 1.

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1-ACYLOXYAZIRIDINE-2,2-DICARBOXYLIC ACID ESTERS

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The reaction of diazomethane and O-acylisonitrosomalonates gave Δ^2-1,2,3-triazoline-5,5-dicarboxylic acid esters, the rates of formation and thermal stabilities of which are determined by the character of ths substituent attached to the oxygen atom. Thermolysis of the triazolines leads to mixtures of 1-acyloxyaziridine-2,2-dicarboxylic acid esters and isomeric dialkyl O-acylisonitrososuccinates; acidolysis with $BF_3 \cdot Et_2O$ makes it possible to obtain exclusively aziridines. The acidic decompositions of dimethyl 4-methyl-Δ^2-1,2,3-triazoline-5,5-dicarboxylate, which was obtained from the reaction of diazoethane and dimethyl O-tosylisonitrosomalonate, leads to dimethyl α-tosyloxyamino-α-vinylmalonate. A dependence of the spin-spin coupling constants (SSCC) of the protons of the aziridine ring on the electronegativities of the substituents attached to the oxygen atom was observed.

Owing to the high pyramidal stability of the nitrogen atom, derivatives of 1-hydroxyaziridine-2,2-dicarboxylic acid esters are ideal subjects for the investigation of the stereochemistry of nitrogen [1]. Enantiomerically pure compounds that have a chiral center only at the nitrogen atom were obtained for the first time in this series [2], and the maximally high barrier to inversion of the nitrogen atom was determined experimentally (31.3 kcal/mole [3]). The principal method for the synthesis of compounds of this class is the reaction of diazomethane with O-substituted derivatives of isonitrosomalonic ester [4].

1-Acyloxyaziridine-2,2-dicarboxylic acid esters are of particular interest. Up until now, only one representative of this series, viz., 1-tosyloxyaziridine, which was obtained by thermolysis or acidolysis (with trifluoroacetic acid) of 1-tosyloxy-Δ^2-1,2,3-triazoline-5,5-dicarboxylic acid ester, was known [4]. However, decomposition of the triazoline in

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